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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
REGION III  
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SUBJECT: Centre Co. Kepone: Technical Basis for  
10 ppb Soil level for Mirex and Kepone

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Attached is technical justification for selection of 10 ppb levels for kepone and mirex in soils. While this may seem very low, some could argue that an even lower number could be recommended. As you will note when you read it some microorganisms are sensitive to levels as low as 0.01 ppb.

Thanks for the opportunity to offer this information and if you have any questions please fell free to contact me.

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TECHNICAL BASIS: 10 ppb Mirex & Kepone in soils

Because of their chemical properties, these compounds require the setting of very conservative residual levels in soil.

- They are very resistant to degradation, with very long residual half-lives.
- They bioaccumulate in the food chain.
- They bioconcentrate in ecological receptors.
- They adversely impact members of both the plant and animal kingdoms.

Both compounds strongly adhere to soil and sediment and are made potentially more available to soil microorganisms with elevated organic carbon. Mirex inhibits photosynthesis in plankton at levels as low as 1 ppb. Some fish are adversely impacted by levels as low as 7 ug/l. Reports indicate that some soil microflora are sensitive to levels as low as 0.01 ug/kg.

Additional technical details are found below.

MIREX:

General Information: Mirex is a fully chlorinated, cage-structured compound. It is resistant to heat (decomposition at 650°C) and has low reactivity with acids, bases and other chemical agents such as ozone and lithium. It is one of the most stable of the organochlorine pesticides known and has been used widely in the southern United States for the control of the imported fire ant. An estimated 74% of the mirex used in the United States for nearly 20 years, however, has been used for nonagricultural uses i.e as a fire retardant in plastics.

Environmental Transport and Fate: The release of mirex in the environment has occurred via effluents from manufacturing plants and sites where mirex was utilized as a flame retardant additive to polymers and at points of application where it was used as an insecticide. Mirex is expected to persist in the environment despite the 1978 ban on its use in the United States. For the most part, mirex is resistant to biological and chemical degradation. Photolysis of mirex may occur. However, sorption is likely to be a more important fate process. Persistent compounds such as kepone and monohydro- and dihydro- derivatives of mirex have been identified as products of extremely slow transformation of mirex. Mirex bioconcentrates in aquatic organisms. It will also adsorb to organic materials

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sorption does not dominate. There is evidence for degradation of mirex to kepone in the environment.

Like kepone, mirex is mobile by virtue of its aliphatic properties. Because of its solubility characteristics, it is not readily transported as a dissolved substance in water and probably moves through the environment dissolved in aliphatic materials and/or adsorbed to particulate matter. Because of its mode of application, atmospheric contamination and dissemination are unlikely. Extensive residue surveys indicate that various factors are instrumental in the distribution of mirex, including: proximity to treated area, rate of decomposition, rainfall patterns, surface runoff, duration of exposure, seasonal population movements, avoidance behavior, trophic relationships and other habitat considerations. Like kepone, mirex thus possesses chemical characteristics that lead to concentration in nontarget terrestrial and aquatic organisms.

Mirex residues are quite persistent in various species. The resistance to mirex degradation and metabolism leads to environmental stability and biomagnification through terrestrial (including the human web) and aquatic systems. However, the fate of mirex in the environment and the associated transfer mechanisms have not been well defined. This situation is further complicated by an inability to account for almost half the mirex sold from 1962 to 1973 and in some cases, the mixing of usage data for flame retardant and fire ant control programs.

Biodegradation: Generally, mirex is resistant to attack by bacteria and fungi and can inhibit the growth of actinomycetes. Although mirex is taken up by microorganisms, plants and higher animals including fish and rats, it is not metabolized. Yet analysis of soils from spills from sites 5 and 12 years after the accidents suggests that dechlorination takes place very slowly and kepone is a biotransformation product of mirex. Both mirex and kepone are highly persistent in the environment and have high lipid:water partition coefficients so that the bioconcentrate several thousand fold in the food chain.

#### Ecotoxicological Profiles:

Aquatic Toxicity: Mirex can be concentrated in fishes directly from sediments, water or food. While photodecomposition products (enhanced by interaction with aliphatic amines) can occur and are presently being used to enhance decomposition in field use, the toxicity of the resulting monohydro, dihydro and trihydro degradation products remains unknown. In addition, certain photodecomposition products accumulated on bait particles leached to seawater and the organisms in a simulated marsh concentrated one of the compounds in a manner similar to mirex itself. Decomposition products must, therefore, be in-

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cluded in any evaluation of the "disappearance" of the parent compound.

The biological significance of mirex is related to its chemical characteristics. Modes of transfer into living systems are important to an understanding of the impact of this insecticide on aquatic organisms. Mirex reduces productivity of green algae. Various species of phytoplankton can concentrate the pesticide and thus may serve as passive agents of transfer to other organisms. Mirex does not appear to have pronounced acute effects on fishes in a range of concentrations found in treated areas. However, dose-dependent secondary effects such as bacterial infection (goldfish) and growth inhibition (bluegills, catfish) appear to be related to mirex accumulation.

Various forms of freshwater and estuarine arthropods are extremely sensitive to mirex, with high mortality at concentrations as low as 0.1 ppb. Juvenile forms are often more susceptible and larval stages of some species show adverse sublethal reactions at concentrations as low as 0.01 ppb. Irritability and mortality have often occurred after exposure. This is the so-called delayed effect which is a distinctive characteristic of mirex in a variety of aquatic species. Although certain factors (age, size, species, physicochemical factors, etc.) influence the form and degree of response (including irritability, loss of equilibrium, paralysis and death), mirex evidently is an effective biocide for various forms of aquatic invertebrates. This should be an important consideration in any evaluation of the environmental impact of mirex.

Bioaccumulation: Routine applications of mirex can kill various nontarget species including oil-loving ants, spiders, beetles and crickets. Uptake and accumulation of mirex can cause reductions in seed germination, seedling emergence and growth in several plant species. This would indicate more pervasive effects than toxicity studies or residue surveys would show. Bioconcentration factors (BCFs) are as follows: algae 12200; fish 2580; snails; 4900; crayfish 16860-71400; daphnids 14650. Bioconcentration factors after 70 days exposure to 0.038  $\mu\text{g/L}$ : grass shrimp 13100-17400; sheepshead minnows: 28900-50000; mud crabs: 15000-18700; hermit crabs: 44800-71100; ribbed mussels (soft tissue): 42000-52600 American oysters, Crassostrea virginica, (soft tissue) 34200-73700.

#### Terrestrial Toxicity:

Mammals: Mirex is lethal as a single dose to rats. It appears not to require metabolism in order to exert its toxicity and, in keeping with this, toxicity does not differ significantly between sexes. Thus, it is likely that it would be similarly toxic to all mammals.

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The subacute toxic effects most commonly observed in mammals have included weight loss, hepatomegaly, and reproductive failure. An important feature of its effect on the liver is the induction of mixed function oxidase.

These effects have been observed at rather low levels of exposure. In rats, 1.0 ppm in the diet caused induction of cytochrome P-450 within 14 days. This is very high in comparison to chronicity factors of 5.4 for DDT and 12.8 for dieldrin, indicating a highly cumulative effect.

Birds: Birds are not extremely sensitive to the acute toxic effects of mirex. However, the relatively high levels of residues in wild birds in the treated areas and the lack of data about the possibility of reproductive effects of mirex on natural populations remains a potential problem. Signs of intoxication in mallards and pheasants from acute oral administration were mild ataxia. Withdrawal signs appeared as soon as 40 minutes after treatment. Mirex fed to captive American kestrels, Falco sparverius, produced a marked decline in sperm concentration with a slight compensatory increase in semen volume resulting in a 70% decrease in sperm numbers. No effect on sperm motility was observed. The survival of Hyalella azteca was reduced relative to that of Crangonyx pseudocracilis during exposure to mirex in water for a 13 day period. This was correlated to greater bioaccumulation of mirex by Hyalella azteca than by Crangonyx pseudocracilis.

Plants: The photosynthesis of plankton is inhibited by 16, 10, 33 and 19% after exposure to 1 ppb after 5, 10, 15 and 20 days, respectively.

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#### KEPONE

General Properties: Kepone is the ketone analog of mirex. Like mirex, it has easily defined physical and chemical properties and saturated, symmetrical molecules. It does not occur in nature. It is released into the atmosphere as a result of its manufacture and use as an insecticide. However, its use as an insecticide has been banned in the United States. Kepone also occurs as a degradation product of. The presence in Kepone of a carbonyl group in place of 2 chlorine atoms in mirex greatly affects Kepone's solubility in water which is 2,000 times that of mirex. It is also more reactive and volatile than mirex. Its thermal decomposition point is about 400°C, compared to about 600°C for mirex. Technical preparations of Kepone contain 94.4% Kepone, with 0.1% hexachlorocyclopentadiene as a minor contaminant.

Environmental Transport and Fate: Kepone released to soil

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adsorbs to the soil; however, some leaching to the groundwater may occur especially in sandy soils with a low organic content. Biodegradation and hydrolysis are not important fate processes but some evaporation may be observed from the soil surface. Kepone released to water adsorbs to sediment and bioconcentrates in fish but may not bioconcentrate in crustaceans or other aquatic organisms. It does not hydrolyze or biodegrade and direct photodegradation is not significant compared to other processes. Evaporation from water is also not significant with a half-life of 3.8 to 46 years predicted for evaporation from a river 1 m deep flowing at 1 m/sec with a wind velocity of 3 m/sec. Kepone released to the atmosphere will not react with photochemically produced hydroxyl radicals or ozone and will be subject to direct photodegradation. Kepone is sorbed to particulate matter in the atmosphere and subject to gravitational settling. Exposure to kepone will occur through the consumption of contaminated food especially contaminated fish and seafood. Exposure may also occur in countries where its manufacture and use as an insecticide are still permitted.

Biodegradation: No evidence of any degradation was detected for Kepone exposed to hydrosols from a reservoir (not previously exposed to kepone) and a creek (contaminated with Kepone) under anaerobic and aerobic conditions for 56 days. No degradation of Kepone exposed to sewage sludge was observed under anaerobic conditions for 120 hr. No degradation was reported for kepone exposed to contaminated James River sediments with added autoclaved silty clay loam soil for 52 days at a pH of 7.0.

Biotic Degradation: Kepone is very stable in the environment and is not significantly hydrolyzed. Photolysis of Kepone in the presence of oxygen results in the formation of carbon dioxide and hydrogen chloride. Irradiation of Kepone dihydrate with UV light, including wave lengths less than 290 nm, caused the formation of 2 compounds which were identical to those formed by the irradiation of mirex.

Bioaccumulation: Kepone is relatively insoluble in freshwater and in seawater. It leaches readily through few soils (highly porous sands), but is adsorbed by clays and loams, especially those with high organic content. Aquatic plant and animal species can be highly efficient in accumulating Kepone, and it is known that a large Kepone reserve can be found in the flesh of fish. The ability of different species to concentrate Kepone varies considerably, however, as a consequence of differences in depuration rates, which can be high in such organisms as oysters and low in some fishes. In general, Kepone is susceptible to transfer from particulate or food-web processes to higher trophic levels with relatively efficient mechanisms for biological magnification, including concentration in humans.

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The bioconcentration Factors (BCFs) are as follows: Pimephales promelas (fathead minnow) 1100- 2200; Cyprinodon variegatus 1548; Leiostomus xanthurus 1221; Palaemonetes pugio 698; Callinectes sapidus 8. Brevoortia tyrannus (atlantic menhaden) 2300-9750; Menidia mendia (Atlantic silverside) 21700-60200.

Soil Adsorption/Mobility: The percent leached through soil cylinders 80 cm deep is: clay loam, 1.2% clay, 17.2% Sandy clay loam, 36.8% sandy loam. Using a reported range of water solubility an estimated range of  $K_{oc}$  of 2400 to 2600 was calculated. A  $K_{oc}$  of this magnitude is indicative of slight chemical mobility and leaching potential in soil.

Toxicity In Sediment: Suspended sediment includes mineral grains, various kinds of plankton and detritus. Each phase concentrates kepone to a different degree. Kepone concentrations in zooplankton sometimes reach levels of 16 ug/g (dry weight) while phytoplankton range from nondetectable to 2.1 ug/g. Kepone associates with the organic portion of the bottom sediments and inorganic grains are relatively clean. Therefore, a change in the ratio of inorganic to organic particles has the potential to change kepone concentrations. Benthic animals may take up kepone directly from the sediments and pass it on to organisms that prey on them.

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